## WGC Technical Database – an immediate success!

The WGC Technical Database (see *Gold Bulletin*, vol 35 (**3**) 2002, page 100) went live on the WGC web site in August 2002. It has proved an immediate hit with scientists and industrialists wanting to keep up-to-date with the latest science and technology of gold. Statistics show about 35,000 visits were made in September and this grew to almost 50,000 visits in October, a month-on-month increase of 14%. Updated quarterly, this searchable Database will next be updated at the end of June.

*Gold Bulletin* is also available on the WGC website and is receiving around 9,000 visits per month. The Technical Database will be found at www.gold.org/value/sci_indu/techdatabase

# Highlights from Recent Literature

### Note:

A more comprehensive list of literature and patents, updated quarterly, will be found in the searchable **Technical Database** on the World Gold Council website, **www.gold.org** under the Science and Industry domain.

## 1 Analytical

### 1.1 Quantitative Electron Microprobe Analysis of Aluminium, Copper, and Gold Thin Films on Silicon Substrates

The thicknesses of aluminium, copper, and gold thin films on silicon substrates were measured by M. Yasuda, S. Yamauchi, H. Kawata, and K. Murata from the Department of Physics and Electronics, Osaka Prefecture University, Sakai, Osaka, Japan, *Journal of Applied Physics,* 2002, **92**(6), 3404, with an electron probe microanalyzer. k ratio versus thickness calibration curves are obtained by a Monte Carlo simulation of electron scattering. The simulation results based on two energy loss models are compared. One is the continuous slowing down approximation model and another is the hybrid model for the discrete and the continuous energy loss processes. Inner shell ionizations and free electron excitations are selected out for the discrete process in the hybrid model. In both models the Mott cross section and the Gryzinski cross section are used for elastic collisions and ionizations, respectively. The exact film/substrate boundary condition is considered. The characteristic and continuum fluorescence corrections are also included in the simulation. The simulation results agree well with experimental ones measured with a quartz oscillator. Effects of the introduction of the discrete energy loss process and the fluorescence correction are discussed and compared.

### 1.2 Cyclic Voltammetry Study of Dopamine Adsorbed on Gold

The objective of this study was to obtain knowledge on the behaviour of dopamine on gold as an electrochemical reagent and adsorbate. S.M. Esquenoni, A.E. Von Mengershausen, S.G. Albano and M.G. Sustersic from the University Nacional de San Luis, San Luis, Argent, *Informacion Tecnologica,* 2002, **13**(4), 57. The redox reaction characteristics of the catechol ring allow the study of the dopamine adsorption under open circuit conditions. The steps of the procedure include adsorption, rinsing with electrolyte, and making cyclic voltammetric scans to detect the amount of adsorbed substance and its electrochemical behaviour. The influence of the anion on the system selectivity with respect to the adsorbate was studied. The behaviour of dopamine was compared with that of other substances having 2 OH groups on the ring (hydroquinone and adrenaline). The adsorption was weak and more layers were formed on the first layer adsorbed. A change in configuration occurs in this step, parallel to perpendicular, with .pi. and .sigma. bonds between the reagent and the metal, respectively.

### 1.3 Characterization of Cold Drawn Gold Bonding Wire with EBSD

Cold drawn gold bonding wires were investigated with electron back scatter diffraction (EBSD). J-H.Cho, J.S. Cho, J.T. Moon, J. Lee, Y.H. Cho, A.D. Rollett and K.H. Oh from Carnegie Mellon University, Pittsburgh, USA, *Materials Science Forum,* 2002, **408-412**(Pt. 1, Textures of Materials), 499. The textures of drawn gold wires contain major <111>, minor <100>, and small fractions of complex fiber components. The <100> oriented regions are located in the center and surface of the wire, and the complex fiber component regions are located near the surface. The <111> oriented regions occur throughout the wire and have large Taylor factors and would be expected to have higher stored energy as a result of plastic deformation compared to the <100> regions. Large misorientations (angles >40.degree.) are located between the <111> and <100> regions, which means that the boundaries between them are likely to have high mobility. Boundaries within the <111> regions are predominantly <111> tilt grain boundaries with large misorientations, similarly, the <100> regions have <100> tilt grain boundaries with smaller misorientations. It appears that the stored energy as indicated by geometrically necessary dislocation content in the subgrain structure is similar in all orientations despite the large differences in Taylor factor

## 2 Catalysis

### 2.1 Nanoscale Catalysis by Gold

A review by G.U. Kulkarni, C.P. Vinod and C.N.R. Rao from the Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore, India, *Surface Chemistry and Catalysis,* 2002, 191. Recent work related to gold catalysis has been discussed addressing the important issue of how the nobleness of gold breaks down at nanometric sizes when in contact with oxidic supports. The high reactivity of gold catalysts in comparison to other metal catalysts is illustrated by reactions such as oxidation of CO and reduction of NO under ambient conditions, as well as epoxidation and hydrochlorination of unsaturated hydrocarbons. Investigations carried out on gold catalysts using a variety of spectroscopy and microscopy techniques are discussed along with the general mechanism of the catalytic process. The observation of maximum reactivity at a cluster size of 2-3 nm, coincident with the size-induced metal to non-metal transition in gold forms the central theme of the article.

### 2.2 Research Progress in Supported Gold Catalysts

A review by progress on precipitation adsorption and catalytic performance, reaction mechanism and active species for supported gold catalysts was reviewed. S.Qi, X. Zou and L. An from the Institute of Applied Catalysis, Yantai University, Yantai, Peoples Republic of China, *Huaxue Tongbao,* 2002, **65**(11), 734. Applications of supported gold catalysts was discussed as well as the basic theoretical problems that require further study.

### 2.3 Carbon Monoxide Low-Temperature Oxidation over Nanosize Gold Catalyst

A review by D. Wang, D. Cheng, Z. Hao and X. Shi from The Research Institute of Chemical Defence, Beijing, Peoples Republic of China, *Huaxue Jinzhan,* 2002, **14**(5), 360. Gold has long been known as being catalytically inactive. However, more interest and attention have been concentrated on the research and development of gold catalysts in recent years. Gold catalysts have been shown good catalytic performances, especially for CO oxidation, and can be used to eliminate CO even below ambient temperature. Compared with other catalysts for CO oxidation, the nanosize gold catalysts have superior catalytic behaviours, such as high catalytic activity, high catalytic stability and high resistance to moisture, and show a continuously increasing and more extensive application prospect. In this review, the preparation factors such as method, support, particle size, pretreatment condition were summarized. The activation and reaction mechanisms were also discussed.

### 2.4 Electrodeposition of Hedgehog-Shaped Gold Crystallites on $TiO_2$ Surface and their Behaviour in Anodic Oxidation of Oxalic Acid

J. Haber, P-I. Nowak and P-I. Zurek from The Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, Krakow, Poland, *Langmuir,* 2003, **19**(1), 196, show that gold may be electrodeposited at surface of $TiO_2$ covered Ti electrode, forming hedgehog-shaped crystallites of well developed surface area. Doping of $TiO_2$ layer by vanadium facilitates the gold electrodeposition, resulting in more uniform and denser distribution of crystallites. At the same time, gold electrodeposition on vanadium-doped $TiO_2$ occurs at lower overpotential in comparison with that of undoped $TiO_2$ layer. In anodic oxidation of oxalic acid, gold deposited at vanadium-doped $TiO_2$ surface behaves in a different manner in comparison with the case of either a massive gold electrode or gold deposited at the undoped $TiO_2$ electrode. In the latter case, the poisoning of the electrode surface by products and/or intermediates of the electrode reaction occurs, whereas no such poisoning is observed in the case of gold deposited at vanadium-doped $TiO_2$ electrode.

### 2.5 Vapor-Phase Carbonylation Process using Supported Gold Catalysts

J.R. Zoeller, A.H. Singleton, G.C. Tustin and D.L. Carver from The Eastman Chemical Company, USA, Patent No. US 6506933, B1 Jan. 2003 describe a vapor-phase carbonylation process, useful for producing carboxylic acids (e.g., acetic acid), esters (e.g., Me acetate), and their mixtures from lower aliphatic alcohols (e.g., methanol), ethers, ester, and ester-alcohol mixtures utilizes a solid-supported catalyst having an effective amount of gold associated with a solid-support material (e.g. Au/C) in the presence of carbon monoxide.

### 2.6 Synthetic Insertion of Gold Nanoparticles into Mesoporous Silica

Industrial catalysts often consist of transition metals supported on microporous or mesoporous high surface area oxides and are prepared by techniques such as impregnation and ion adsorption. In standard fabrication processes the metal particle size is not well-controlled. In this paper the authors, Z. Konya, V.F. Puntes, I. Kiricsi, J. Zhu, J.W. Ager, M.K. Ko, H. Frei, P. Alivisatos and G.A. Somorjai, from the Department of Chemistry, University of California at Berkeley, USA, *Chemistry of Materials,* 2003, **15**(6), 1242, report a new synthetic route for the production of catalyst materials with more precise control of the metal particle size. Gold nanoparticles encapsulated in mesoporous silica (MCM-41 and MCM-48) served as a model system, although the techniques described are applicable to a wide variety of metals and oxide supports. The samples were characterized by a combination of low-angle powder X-ray diffraction, transmission electron microscopy, N2 porosimetry, IR spectroscopy, and X-ray absorption near-edge spectroscopy. The results show that the MCM-41 and MCM-48 structures retain their long-range order when metal particles are added; in addition, the size of the channels increases monotonically with metal loading. X-ray absorption near-edge spectroscopy in combination with the adsorption of thiols provides conclusive evidence that 2- and 5-nm-diameter Gold nanoparticles are incorporated into the pores of the silicates and that they are accessible to reactant molecules.

### 2.7 Gold Nanoparticles Deposited on $SiO_2$/Si(100): Correlation between Size, Electron Structure, and Activity in CO Oxidation

Nanosize gold particles were prepared by Ar+ ion implantation of 10-nm thick gold film deposited onto a $SiO_2$/Si(100) wafer possessing no catalytic activity in the CO oxidation. L. Guczi, G. Petoe, A. Beck, K. Frey, O. Geszti, G. Molnar and C. Daroczi from the Department of Surface Chemistry and Catalysis, Chemical Research Center, Budapest, Hungary, *Journal of the American Chemical Society,* 2003, **125**(14), 4332. Along with size reduction the valence band of the gold particles and the actual size were detected by UV- and XPS (UPS, XPS) and by transmission electron microscopy (TEM) as well as atomic force microscopy (AFM), respectively.

The catalytic activity was detected via CO oxidation. Energy distribution of the photoelectrons excited from 5d valence band of gold was strongly affected by Ar+ implantation. This variation was interpreted by the redistribution of the valence band d. of states (DOS). The intrinsic catalytic activity of the gold particles increased with decreasing size. When an Au/FeOx interface was created by FeOx deposition on large gold nanoparticles, a significant increase in the rate of the CO oxidation was observed.

### 2.8 Characterization of Supported Gold Catalysts with $^{197}$Au Moessbauer Effect Spectroscopy

A. Goossens, M.W.J. Craje, A.M. van der Kraan, A. Zwijnenburg, M. Makkee, J.A. Moulijn, R.J.H. Grisel, B.E. Nieuwenhuys and L.J. de Jongh from the Kamerlingh Onnes Laboratorium, Universiteit Leiden, Netherlands, *Hyperfine Interactions,* 2002, **139/140**(1-4/1-4), 59, report on a $^{197}$Au Moessbauer study of several types of supported gold catalysts. Differences in particle size show up in the Moessbauer spectra by a change in the relative wt. of the spectral contribution of the surface atoms. The presence of ionic gold in active gold catalysts is not observed. The spectra can be interpreted in terms of bulk-like contributions from the inner-core atoms plus contributions from the outermost atoms at the surface of the particles.

## 3 Chemistry

### 3.1 Self-assembled Molecular films of Tetraamino metal (Co, Cu, Fe) phthalocyanines on Gold and Silver. Electrochemical and Spectroscopic Characterization

The formation of molecular films of 2,9,16,23-tetraamino metal phthalocyanines [TAM(II)Pc; M (II) = Co, Cu, and TAM(III)Pc; M = Fe] by spontaneous adsorption on gold and silver surfaces is described by M.P. Somashekarappa, J. Keshavayya and S. Sampath from the Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore, India, *Pure and Applied Chemistry,* 2002, **74**(9), 1609. The properties of these films have been investigated by cyclic voltammetry, impedance, and FT-Raman spectroscopy. The charge associated with Co(II) and Co(I) redox couple in voltammetric data leads to a coverage of (0.35 .+-. 0.05) .times. 10-10 mol $cm^{-2}$, suggesting that the tetraamino cobalt phthalocyanine is adsorbed as a monolayer with an almost complete coverage. The blocking behaviour of the films toward oxygen and Fe(CN)63-/4- redox couple have been followed by cyclic voltammetry and impedance measurements. This leads to an estimate of the coverage of about 85% in the case of copper and the iron analogs. FT-Raman studies show characteristic bands around 236 $cm^{-1}$ revealing the interaction between the metal substrate and the nitrogen of the $-NH^2$ group on the phthalocyanine molecules.

### 3.2 Digestive-Ripening Agents for Gold Nanoparticles: Alternatives to Thiols

Several ligands, such as alkylthiols, -amines, -silanes, -phosphines, -halides, and simple alkanes, were used for digestive ripening, a process in which a colloidal suspension in a solvent is refluxed at the solvent boiling temperature in the presence of a surface-active ligand to convert a highly polydisperse colloid into a nearly monodisperse one. B.L.V. Prasad, S.I. Stoeva, C.M. Sorensen, K.J. Klabunde from the Department of Chemistry, Kansas State University, USA, *Chemistry of Materials,* 2003, **15**(4), 935. Apart from thiols, which are the only established digestive-ripening ligands, amines, silanes, and phosphines were found to be similarly efficient for this purpose. The important steps involved in the digestive ripening were identified to be (1) breaking the polydisperse colloid into smaller size particles upon addition of the ligand, (2) isolating this colloid from the reaction side products, and finally (3) heating this isolated colloid in the presence of the ligand to form a nearly monodisperse colloid.

The successful ligands could be differentiated from the others based on their effectiveness to perform the different tasks in each step. Namely, they broke the bigger nanoparticles into smaller ones in the first step, formed a stable redispersible colloid in toluene after the second step, and at the end of the third step lead to a nearly monodisperse colloid. The ability of the different ligands to break the bigger, prismatic as-prepared particles in the first step varied as RSH .apprxeq. RNH2 .apprxeq. R3P .apprxeq. RSiH3 > RI > ROH .apprxeq. RBr and simple alkanes completely failed to induce any changes in the size and shape of the as-prepared colloid. Ligands such as RI, RBr, and ROH failed in the second step, possibly because of the poor ligand-gold interaction. The ligand-gold interaction trends observed here could be rationalized semiqualitatively by invoking the hard and soft acid and base theory, which suggests that a soft acid-like gold likes to interact with softer bases such as RSH and R3P rather than hard bases such as ROH. After the third step, the sizes of the nearly monodisperse particles depended on the ligand used for digestive ripening and correlated well with the ligand-gold interaction trends.

### 3.3 The Adsorption of Gold and Copper onto Ion-Exchange Resins from Ammoniacal Thiosulfate Solutions

The recovery of gold and copper from ammonium thiosulfate solutions using anion-exchange resins has been investigated using batch studies. H. Zhang and D.B. Dreisinger from the Department of Metals and Materials Engineering, The University of British Columbia, Vancouver, BC, Canada, *Hydrometallurgy,* 2002, **66**(1-3), 67. Strongly basic resins are preferred to weakly basic resins because of their greater range of operational pH and higher loading. The kinetics and isotherms for the adsorption of gold and copper were measured. Individually, gold and copper can be loaded onto resins at high concentrations. Copper greatly decreased stability of the ammonium thiosulfate solution due to copper-catalyzed thiosulfate oxidation and formation of copper sulfides or hydroxides, depending on the conditions. Tetrathionate, as the product of thiosulfate oxidation, strongly poisoned the resins. The effect of thiosulfate and ammonia concentrations on the adsorption was also studied. During simultaneous loading, selectivity for gold over copper was obtained. The metals were eluted with a mixed solution of $Na_2SO_3$ and $NH_3$.

## 4 Electrochemistry

### 4.1 Electron and Ion Transfer through Multilayers of Gold Nanoclusters covered by Self-Assembled Monolayers of Alkylthiols with Various Functional Groups

The electrochemical characteristics of various kinds of multilayers of gold nanoclusters (GNCs) were investigated. K. Uosaki, T. Kondo, M. Okamura and W. Song from the Graduate School of Science, Hokkaido University, Sapporo, Japan, *Faraday Discussions,* 2002, 121(Dynamic Electrode Surface), 373. Two types of gold nanoclusters, one covered by self-assembled monolayers (SAMs) of mercaptoundecanoic acid (MUA), hexanethiol (C6SH), and ferrocenylhexanethiol (FcC6SH), MHF-GNC, and the other with MUA and C6SH, MH-GNC, were used. The multilayers were constructed on a gold(111) surface based on a carboxylate/metal cation (Cu++)/carboxylate or carboxylate/cationic polymer (poly(allylamine hydrochloride):PAH)/carboxylate electrostatic interaction. While the multilayers constructed by the former method were stable only in non aqueous solutions, those constructed by the latter method were stable even in aqueous solutions. Electrochemical measurements of the multilayers of MHF-GNCs showed a pair of waves corresponding to the redox of the ferrocene group around 350-480 mV and the charge of these peaks, i.e., the amount of adsorbed GNC, increased linearly with the construction cycle up to 6 cycles in the former and to 18 cycles in the latter. A reversible redox response of the ferrocene moiety was observed even at the gold electrodes with five GNC layers of two different sequences in which MHF-GNC exists as the layer closest to the gold electrode. These results show the facile transfer of electrons and ions through the multilayers of the SAM-covered GNCs and electron transfer between the ferrocene moiety and the gold(111) electrode takes place through the GNC cores by hopping.

### 4.2 Electroless Gold Plating Bath and Method of Gold Coating of Printed Wiring Board or Indium Tin-Oxide (ITO) Substrate

This invention by K. Suda, from the PA Shipley Co. L.L.C., USA Patent No JP 2003013248, A2 on 15th Jan 2003 investigates the electroless gold plating bath method. Electroless gold plating baths and plating methods using these baths are provided, whereby base metal etching or erosion arising when gold is deposited on the material to be plated is extremely slight, so that a gold film with good adhesion, and good soldering strength is obtained. The electroless gold plating bath includes (a) water-soluble gold compound (esp. 2 g/L of potassium gold cyanide), (b) 0.005-0.5 mol/L of complexing agent (e.g., ethylenediaminetetramethylenephosphonic acid) that stabilizes gold ions in the plating bath, but does not cause substantial dissolution of nickel, cobalt or palladium in the plating bath, (c) 0.01-100 g/L of a polyethyleneimine compd., and (d)

.gtoreq.1 additive selected from pH stabilizer, lustre agent, wetting agent, and reducing agent. When a material to be plated is subjected to such a gold plating bath, corrosion of the base metal under the surface of the plated material is reduced by controlling the substitution reaction rate immediately after initiation of the reaction, and adhesion between the base metal and deposited gold coating is increased.

### 4.3 Preparation, Characterization and Application of Alkanethiol Self-Assembled Monolayers Modified with Tetrathiafulvalene and Glucose Oxidase at a Gold Disk Electrode

In this work, the results obtained with a gold disk electrode modified with alkanethiol self-assembled monolayers (SAMs), and glucose oxidase (GOD), and the redox mediator tetrathiafulvalene (TTF) immobilized atop are presented. S. Campuzano, R. Galvez, M. Pedrero, F.J.M. De Villena and J.M. Pingarron from The Universidad Complutense de Madrid, Madrid, Spain, Proceedings - Electrochemical Society, 2001, 2001-18(Chemical and Biological Sensors and Analytical Methods II), 602. A gold electrode modified with a mercaptopropionic acid SAM, where GOD and TTF were immobilized by crosslinking with glutaraldehyde, allowed linear calibration curves for glucose, obtained by amperometry in stirred solutions at an applied potential of +0.20 V, in the 5.0 10-6 - 1.0 10-2 mol L-1 range. A detection limit of 1.3 10-6 mol L-1, and a RSD of 5.2% (n=10), at a concentration level of 1.0 10-4 mol L-1, were found. No leaching of the enzyme and mediator is observed during the whole day. The modified electrode is stable in dry conditions for 24 h and for at least 100 h if kept in a 4.degree.C H2PO4-/HPO42- buffer solution (pH 7.4).

## 5 Electronics and Sensors

### 5.1 Design of a Semiconductor Device having Gold Bump Electrodes

The invention by J.K. Fang, C.H. Chiang, S.K. Chen and C.F. Weng from the Advanced Semiconductor Engineering, Inc., Taiwan, Patent No. US2002190395, A1, relates to the design of a semiconductor device having gold bump electrodes, where the underbump metallurgy uses a titanium wetting layer to provide better etching selectivity and reduce costs. The device consists of a dielectric layer formed atop a substrate which contains an aluminium contact pad, where at least a portion of the contact pad is exposed through the dielectric layer. The aluminium contact pad has an underbump metallurgy which includes an aluminium layer formed on the exposed portion of the aluminium contact pad, a nickel-vanadium layer formed on the aluminium layer, and a titanium layer formed on the nickel-vanadium layer. A gold bump formed on the titanium layer acts as the bump electrode.

### 5.2 Photoluminescent and Electronic Properties of Nanocrystalline Silicon Doped with Gold

Doping nanocrystals Si (nc-Si) films grown by laser ablation with gold leads to a considerable suppression of the nonradiative recombination of the charge carriers and excitons, an increase in the intensity and stability of the visible photoluminescence, and enhancement of the low-energy (1.5-1.6 eV) photoluminescence band. E.B. Kaganovich, I.M. Kizyak, S.I. Kirillova, E.G. Manoilov, V.E. Primachenko, S.V. Svechnikov and E.F. Venger, from The National Academy of Sciences of Ukraine, Kiev, 03028, Ukraine, *Semiconductors (Translation of Fizika i Tekhnika Poluprovodnikov* (*Sankt-Peterburg*)) 2002, **36**(9), 1027. In gold-doped samples, the magnitude of the photovoltage and the rate of electron capture by traps in the film are reduced, and the d. of boundary electron states and the concentration of deep electron traps at the single-crystal Si (c-Si) substrate are decreased as well. The observed effect of doping on the photoluminescent and electronic properties of nc-Si films and nc-Si/c-Si structures is caused by the passivation of dangling Si bonds with gold and by the further oxidation of Si at the surface of nanocrystals, which gave high-barrier $SiO_2$ layers.

### 5.3 Gold-Based Electrical Interconnections for Microelectronic Devices

A method of making an electric interconnection from a microelectronic device (to a package) is described by the inventors K.A. Peterson, S.E. Garrett, C.A. Reber and R.D. Watson from the Sandia Corporation, US. Patent No. US 6500760, B1, 31 December 2002. The invention entails providing a microelectronic device having Si surface, ball or wedge compression bonding a gold-based conductor directly to a Si surface, such as a polysilicon bonding pad in a MEMS or IMEMS device, without using layers of Al or Ti disposed in-between the conductor and the Si surface, holding the bond at T >eutectic temperature of a liquid eutectic phase comprising gold and Si. A method of attaching a gold-based bump to a microelectronic device is also described and a method of flip-chip bonding a microelectronic device to a package.

A method of packaging a MEMS device is described entailing (a) providing an unreleased MEMS device fabricated on a die, the MEMS device comprising a plurality of polysilicon bonding pads; (b) providing a package comprising a plurality of corresponding package bonding locations; (c) die attaching the die to the package; (d) providing a plurality of gold-based elec. conductors; (e) making an elec. interconnection between the MEMS device and the package by compression bonding one end of a gold-based conductor directly to a polysilicon bonding pad, without using an aluminium or titanium layer disposed in-between the conductor and the pad, and then bonding the other end of the conductor to the corresponding package bonding location; (f) moving to another pad on the MEMS device after step (e); (g) repeating steps (e), and then (f), until all of the bonding locations have been interconnected; and (h) releasing the MEMS device.

### 5.4 Soldering of Gold in Microelectronics Products by Sn-In Solders

Tin-based solders intended for soldering semiconductor device components are analyzed by V.V. Zenin, G.L. Polner, V.N. Belyaev and Y.E. Segal from the Voronezh. Gos. Tekh. University, Voronezh, Russia, *Izvestiya Vysshikh Uchebnykh Zavedenii, Elektronika,* 2002, **3**, 30. The results of studies on dissolution of a gold microwire with 0.04 mm diameter in a POIn50 solder during soldering of hybrid integrated circuits (HIC) and microassemblies are presented. The dissolution of the gold wire was considered as a function of the soldering temperature and time, as well as on the time of holding the soldered joint at 100.degree.C. The interaction of the POIn50 solder with a gold coating of superhigh-frequency and HIC plates when soldering on metal substrates was analyzed.

### 5.5 Avoiding Adhesion problems. Adhesion of thin Gold layers on $SiO_2$ is improved through Tempering

The improvement of gold adhesion on $SiO_2$ by tempering was studied by K. Schambach, K. Eden, K. Schumacher, J. Horstmann, G. Wiegleb and C. Horst. *Metalloberflaeche,* 2002, **56**(11-12), 31

Experiments were performed with p-doped Si-wafers <100> coated with a tetra-Et orthosilicate (TEOS) oxide layer and further sputtered with gold layers of 20-60 nm thickness. The wafers were tempered in a $N_2$-atmosphere for 60 min at 450, 500, 600, and 750.degree and for 15 and 20 min at 415.degree. After the 60 min tempering a good gold layer adhesion was detected in adhesive tape tests but the gold layers showed no electric conduction. After tempering for 15 and 20 min the gold layers were electrically conductive and the adhesion increased with decreasing gold layer thickness. In further experiments the adhesion of the gold layer with an additional $SiO_2$ protection layer was tested under different tempering and protection layer application conditions. After 2-fold tempering before and after the application of the protection layer at 415.degree the gold layers were conductive and adhesive. The optimal tempering temperature and duration depended on thickness and structure of the gold layer.

### 5.6 Gold or Gold Alloy Clad Wire for Bonding Electronic Circuits

The inventors T. Arikawa and K. Ishizuka from the Tanaka Electronics Industry Co., Japan, Patent No. JP 2003045909, A2 14 February 2003, describe a coating material made from high-purity gold or gold alloy is clad to a core from high-purity Zn or Zn alloy, high-purity Sb or Sb alloy, or high-purity In or In alloy to obtain a gold or gold alloy clad wire for bonding electronic circuits, wherein the content of Zn, Sb or In is 0.1-30% when the clad wire is dissolved and solidified. At least one side of the bonding place of the electronic circuits is a thin film pad on glass substrate. The gold or gold alloy clad wire has good bondability and drawability.

## 6 Medical and Dental

### 6.1 Comparison of Gold-Coated NIR Stents with Uncoated NIR Stents in Patients with Coronary Artery Disease

A multi-centre, prospective, randomized trial was conducted to detect whether gold-coating increases in-stent restenosis in patients with coronary artery disease. S-J. Park, C.W. Lee, M-K. Hong, J-J. Kim, S-W. Park, S-J. Tahk, Y.S. Jang, K.B. Seung, J-Y. Yang and M.H. Jeong from the Department of Medicine, Asian Medical Center, University of Ulsan, Seoul, S. Korea, *American Journal of Cardiology,* 2002, **89** (7), 872. Between Oct. 1999 and July 2000, 216 consecutive patients scheduled for elective stenting were enrolled for this study at 6 centres in Korea. Eligible patients were randomly assigned to receive either an uncoated NIR stent or a gold-coated NIR stent according to computer-generated randomization lists. Gold coating may not have an impact on stent thrombosis but may increase the risk of restenosis after coronary stenting. These results indicate that gold coating may trigger an exaggerated vascular response after coronary stenting. Gold is a highly biocompatible material, and thus suitable for use in the biomedical field. Gold deserves consideration as an attractive candidate for stent coating, which improves the visibility of stents and facilitates stent deployment at the desired position. The gold-coated NIR stents elicited greater restenosis than uncoated stainless steel NIR stents, supporting the theory that gold may exaggerate neointimal hyperplasia within the stents.

### 6.2 In Vivo Liberation of Gold Ions from Gold Implants. Autometallographic Tracing of Gold in Cells adjacent to Metallic Gold

The implantation of small pieces of gold has been used as an unauthorized remedy for osteoarthritis and pain. The aim of the study by G. Danscher from the Department of Neurobiology, University of Aarhus, Denmark, *Histochemistry and Cell Biology,* 2002, **117**(5), 447, was to evaluate whether gold ions are released from gold implants. Pieces of pure gold were placed in the connective tissue of skin, bone and brains of anesthetized animals. Ten days to several months later the animals were anesthetized and killed by transcardial perfusion. Tissue blocks containing the gold pieces were cut, and the sections were silver-enhanced by autometallography. It was found that gold ions are released from the implanted gold and diffuse out into the surrounding tissue. The gold-containing cells in connective tissues were macrophages, mast cells and fibroblasts. In the brain, gold accumulated in astrocytes and neurons. Proton-induced X-ray emission spectroscopy analysis of the tissue surrounding gold implants confirmed that gold ions are liberated. The findings suggest that the gold implant technique, on a local scale, mimics systemic treatment with a gold-containing drug.

### 6.3 Gold Coating of Nitinol Devices for Medical Applications

A process has been developed by R. Steegmueller, C. Wagner, T. Fleckenstein and A. Schuessler from EUROflex Schuessler GmbH, Germany, *Materials Science Forum,* 2002, **394-395**(Shape Memory Materials and Its Applications), 161, to directly plate gold on Nitinol components to improve the radiopacity of medical devices such as filters and stents. The authors discuss coating structure, advantages and limits of electroplating techniques of gold on Nitinol, which allows a wet-to-wet process following electropolishing of Nitinol. The composition of the extremely pure gold coatings is investigated by surface analysis methods such as SIMS and SMNS. The adhesion of the gold layer on Nitinol and its ductility to deform with the component is investigated by scratch tests and device performance tests. The potential danger of embrittlement by low amounts of Hydrogen in the Nitinol is addressed by Hydrogen analysis of gold coated components. The corrosion behaviour of gold plated Nitinol components is discussed based on literature data.

## 7 Metallurgy, Materials and Coatings

### 7.1 Transmission Surface-Plasmon Resonance (T-SPR) Measurements for Monitoring Adsorption on Ultrathin Gold Island Films

Evaporation of ultra thin (1.3-10 nm nominal thickness) gold films onto quartz or mica leads to the formation of a layer of uniform gold islands on the transparent support. G. Kalyuzhny, A. Vaskevich, M.A. Schneeweiss and I. Rubinstein from the Weizmann Institute of Science, Rehovot, Israel, *Chemistry--A European Journal,* 2002, **8**(17), 3849. The morphology of these films was studied using atomic force microscopy (AFM) and SEM (SEM) imaging. The surface plasmon (SP) absorption characteristic of such films is highly sensitive to the surrounding medium, with the plasmon band changing in intensity and wavelength upon binding of various molecules to the surface. The binding process can be monitored quantitatively by measuring the changes in the gold SP absorption using transmission UV/Vis spectroscopy. The method, termed transmission surface plasmon resonance (T-SPR) spectroscopy, is shown, by the authors, to be applicable to both chemically and physically adsorbed molecules, in liquid or gas phase, with measurements carried out either ex situ or in situ (real-time measurements) using a variety of molecular probes. Binding to a preformed molecular layer on the gold surface produces a similar response, suggesting the possible use of T-SPR for selective sensing. The sensitivity of T-SPR-spectroscopy in detecting molecule binding to the gold depends strongly on the film preparation conditions, and may be comparable to that obtained in surface plasmon resonance (SPR) sensing.

## 8 Nanotechnology

### 8.1 Liquid Crystalline Assemblies of ordered Gold Nanorods

Gold nanorods have been prepared in aqueous solution using a seed-mediated growth approach in the presence of surfactant. N.R. Jana, L.A. Gearheart, S.O. Obare, C.J. Johnson, K.J. Edler, S. Mann and C.J. Murphy from the Department of Chemistry and Biochemistry, University of South Carolina, Columbia, SC, USA, *Journal of Materials Chemistry,* 2002, **12**(10), 2909 . The authors observed the formation of liquid crystal phases in concentrated solutions of high aspect ratio (13-18) gold nanorods by polarizing microscopy, transmission electron microscopy, and small angle X-ray scattering. These phases, which are stable up to 200.degree.C, exhibited concentration-dependent orientational order.

### 8.2 Sintering of Alkanethiol-Capped Gold and Platinum Nanoclusters

One of the unusual properties of metal nanoclusters is the size dependence of the melting temperature. Studies by J.E. Martin, J. Odinek, J.P. Wilcoxon, R.A. Anderson and P. Provencio from Sandia National Laboratories, Albuquerque, NM, USA, *Journal of Physical Chemistry B,* 2003, **107**(2), 430, show that the melting temperature is a decreasing function of the cluster diameter, although the actual dependence is not known, due to the difficulties associated with the experimental measurements. The authors synthesized narrow dispersity alkanethiol-functionalized gold and platinium nanoclusters in inverse micellar solutions and have measured the sintering temperatures of these films using a capacitance technique to detect the onset of film conditions. Cluster sintering is accompanied by pronounced optical changes and a thermal signature that can be observed in DTA. The large optical absorbance of nanocluster films makes laser sintering a practical method for the formation of metalization layers.

## 8.3 Synthesis of Nanorattles Composed of Gold Nanoparticles Encapsulated in Mesoporous Carbon and Polymer Shells

In this study the authors fabricated new spherical silica templates with submicrometer sized solid cores containing an encapsulated gold nanoparticle surrounded by a mesoporous shell structure. M. Kim, K. Sohn, H.B. Na and T. Hyeon from the National Creative Research Initiative Center for Oxide Nanocrystalline Materials and School of Chemical Engineering, Seoul National University, Seoul, S. Korea, *Nano Letters,* 2002, **2**(12), 1383. Hollow spherical carbon and polymer capsules, containing gold nanoparticles were synthesized using these silica templates. The resulting carbon capsules inversely replicated the structure of the silica template and contained uniform pores with a narrow pore size distribution centered at 3.8 nm. These carbon capsules exhibited a BET surface area of >1000 $m^2$ $g^{-1}$ and a total pore vol. of >1.0 $cm^3$ $g^{-1}$. In addition, hollow polymer capsules having a well-defined pore size were fabricated using a similar synthetic procedure.

## 8.4 Photothermal Patterning of Microgel/Gold Nanoparticle Composite Colloidal Crystals

The authors, C.D. Jones, A.L. Lyon from The School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, USA, *Journal of the American Chemical Society, 2000*, **125**(2), 460, present a new method for laser direct writing in self-assembled hydrogel microparticle colloidal crystals via photothermal excitation of co-assembled colloidal gold particles. Close-packed colloidal crystals are assembled from approximately 224 nm diameter, thermo-responsive, poly(N-isopropylacrylamide) hydrogel microparticles (microgels); these crystals display sharp Bragg diffraction peaks in the mid-visible region of the spectrum due to the periodic dielectric function of the assembly. Raising the temperature of the crystal above the characteristic volume phase transition temperature of the microgel particles, results in a reversible melting of the crystalline material due to the particle-based deswelling event. This transition can be used either to anneal defects from the crystalline material or to controllably and reversibly convert the assembly from the coloured, crystalline state to a nondiffracting glassy material. Crystal-to-glass transitions are similarly accomplished via photothermal excitation when 16 nm diameter colloidal gold particles are co-assembled with the responsive microgels. Excitation of the colloidal gold plasmon absorption with a frequency doubled Nd:YAG laser (.lambda. = 532 nm) results in optically directed conversion of either glasses to crystals or crystals to glasses, depending on the initial state of the assembly and the illumination time. These results represent a fundamentally new method for the patterning of self-assembled photonic materials.

## 8.5 Controlled Assembly of Nanoparticle-Containing Gold and Silica Microspheres and Silica/Gold Nanocomposite Spheroids with Complex Form

A. Kulak, S.A. Davis, E. Dujardin and S. Mann from the School of Chemistry, University of Bristol, UK, *Chemistry of Materials,* 2003, **15**(2), 528.

Sonication of microliter volumes of aqueous silica, gold, or silica/gold colloids in toluene results in solidification within dissolving water droplets and the facile preparation of nanoparticle-based microspheres. At 0 and 10 .degree.C, smooth spheres with mean diameters of 0.5 and 0.75 .mu.m, respectively are produced for samples prepared from gold or silica nanoparticles. In contrast, nanocomposite spheroids prepared from 2:1 silica/gold mixtures exhibit unusual surface textures due to higher-order aggregation between microspheres undergoing solidification. At 0 .degree.C, binary collisions between similar sized droplets produce fused pairs that solidify and subsequently fragment into 0.5-.mu.m-sized silica/gold microspheres with a pitted olive morphology consisting of a single circular indentation.

## 8.6 Control of Particle Size in the Preparation of Colloidal Gold

The preparation of colloidal gold is a subject of practical interest in many technology fields. It is generally accomplished by reduction of $HAuCl_4$ solution with sodium citrate which is known to be influenced by several factors such as temperature and reactants concentration. In the course of the present investigation, the rate of addition of sodium citrate was observed to play a very important role on the particle size distribution. The studies by S.M. Saraiva and J.F. De Oliveira from the Department of Metallurgical and Materials Engineering-Federal University of Rio de Janeiro, Brazil, *Journal of Dispersion Science and Technology,* 2002, **23**(6), 837, including UV/visible absorption spectrophotometry, light scattering, and transmission electron microscopy (TEM) showed that the higher the rate of addition of sodium citrate, the smaller is the mean particle size and the narrower is the diameter of the gold particles produced.

## 8.7 Preparation of Gold Nanoparticles by High-Pressure Method with Polyacrylamide in Microwave Oven

The diameters of gold nanoparticles in dark-red, purple, and blue-violet colors were 8.3, 30, and 60 nm, respectively, A.M. Qin, Z.L. Jiang, J.M. Zou, L.S. Wang, L. Liao and W.Q. Yin from Department of Resource and Environmental Science, Guangxi Normal University, Guilin, Peoples Republic of China, *Yingyong Huaxue,* 2002, **19**(12), 1150. The maximum peak in UV absorption spectra was at 524 nm and 542 nm for dark-red and purple gold particles, respectively, while their maximum peaks in resonance scattering spectra were at 570 nm and 550 nm, respectively. Two absorption peaks were observed: 530 nm and 620 nm for blue-violet gold nanoparticles, whose maximum resonance scattering peak was found at 550 nm. A solution of dark-red gold nanoparticles with diameter of 8.3 nm in concn. of [Au] < 5.0 .times. $10^{-4}$ g/L could be obtained from a solution of PAAm and Au(III) at m(PAAm)/m(Au(III)) = 19. The procedure has advantages of rapidity and convenience and can afford red gold nanoparticles with uniform distribution and good stability.

# 9 Refining

## 9.1 The Treatment of Copper-Gold Ores by Ammonium Thiosulfate Leaching

The application of ammonium thiosulfate to the treatment of copper-gold ores has been investigated by E. Molleman and D. Dreisinger from the Department of Metals and Materials Engineering, The University of British Columbia, Vancouver, Canada, *Hydrometallurgy,* 2002, **66**(1-3), 1. Copper minerals and copper-gold samples, were leached in an ammonium thiosulfate solution under varying experimental conditions of aeration, temperature and reagent addition. The behaviour of thiosulfate, tetrathionate and sulfate in solution was studied by using ion chromatography. Both gold extraction and thiosulfate stability are affected by the combination of aeration and cupric ions in solution. The authors state that it is important to establish a balance between providing sufficient air and cupric ions for rapid gold dissolution and at the same time minimize the amount of air in the presence of cupric ions to prevent excessive thiosulfate degradation. Promising results of high gold extractions and low thiosulfate consumption were obtained during a 24-h leach without forced aeration.

## 9.2 Method for Extracting Gold from Ore

A.P. Tatarinov, S.S. Gudkov, A.F. Rashchenko, Y.E. Emel'yanov and V.E. Dement'ev, Patent No. RU 2185453, C1, July 2002, describes a method for extracting gold from ore. The method involves grinding ore; treating with cement; pelletizing; piling and leaching gold from pile. Prior to treating with cement, ground ore is subjected to concentration for obtaining enriched and depleted parts. Upon cyaniding of enriched part, produced cakes are mixed with depleted part.

## 9.3 Recovering Gold from Thiosulfate Leach Pulps via Ion Exchange

M.J. Nicol and G. O'Malley from The A.J. Parker Cooperative Research Center for Hydrometallurgy, Murdoch University, Perth, Australia, *JOM,* 2002, **54**(10), 44, describe how the thiosulfate process lacks a proven in-pulp method of recovering the dissolved gold because activated carbon is not effective for absorption of the gold-thiosulfate complex. The effectiveness of commonly available anion exchange resins for the recovery of gold from thiosulfate leach liquors and pulps was evaluated. Strong-base resins are the preferred choice for gold recovery because they have a higher gold loading capacity than weak-base resins. Amberjet 4200 exhibited a high selectivity for the gold-thiosulfate complex over other metal anions in solution. Small-scale countercurrent absorption runs in a six-stage mini plant with the strong-base resin achieved satisfactory gold loading and acceptable barrens.

## 9.4 Reaction Chemistry of Gold Leaching in Thiourea Solution for a Turkish Gold Ore

A finely disseminated gold-bearing ore from Kaymaz, Turkey was processed by S. Orgul and U. Atalay from the Mining Engineering Department, Middle East Technical University, Ankara, Turkey, *Hydrometallurgy,* 2002, **67**(1-3), 71. The main objective was to detect the mechanism of reaction between thiourea and $Fe^{3+}$ in the thiourea leaching of gold. Thiourea consumption levels were also examined during the leaching operations for different leaching parameters, i.e., molar ratio of ferric sulfate/thiourea, pH, and temperature. Leaching using the thiourea process was compared with cyanidation. Under optimum leach conditions, 85.8% gold extraction was obtained with feed of -53 .mu.m particle size in 6 hours.

# 10 General

## 10.1 Computer Recycling: A Virtual Gold Mine for Silver Recovery

A review in French by M. Mardones, D. Miousse, B. Ponsard, S. Alex, D. Espinoza, Daniel from INTEC Santiago, Chile, *Vecteur Environnement,* 2002, **35**(6), 83. Manufacturers and users of computers are faced with issues of recycling used computers. Computers are composed of 16% of plastics, 13% of glass, 16% of plastics/glass fibers/silicon from printed circuit boards, 1-2% of plastic/copper from cables and 52% of metal from disks and metallic parts. Recycling of printed circuit boards is the most interesting part economically due to relatively high content in precious metals (such as 800 g/ton of waste in Ag, 260 g/ton of Au, 100 g/ton of Pd and 150 kg/ton of Cu). The recovery of those precious metals is done by hydrometallurgical process.